Effects of Mixing Techniques on Glass-Ionomer Cements

Undergraduate Research Thesis

Presented in partial fulfillment of the requirements for graduation *with honors research distinction* in Microbiology in the undergraduate colleges of The Ohio State University.

by

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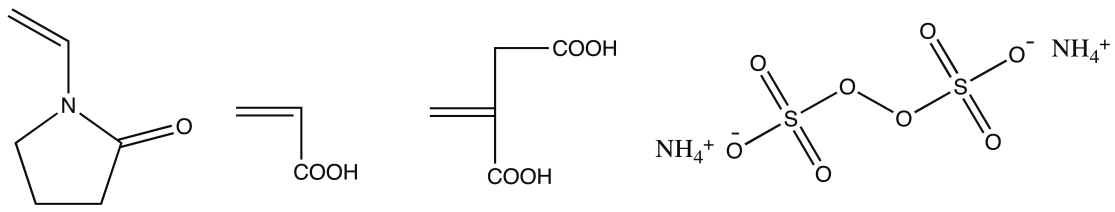
1. Introduction

Glass-ionomer cements (GICs) are a dental restorative and were first introduced in 1971 by Wilson and Kent in the Laboratory of the Government Chemist in London.[1] GICs are currently used worldwide as an alternative to the more common amalgam (silver) fillings and composite resins in repairing dental cavities caused by tooth decay. GIC differ from resin modified glass-ionomer cements (RMGIC), which involve a photochemical free radical cure component.[2] One major benefit that glass-ionomers have that other restorative materials lack is the ability to emit fluoride directly onto the tooth structure. This has numerous benefits including, but not limited to, inhibiting secondary caries, adhesion to tooth structure, protection against decalcification, decreased dentin hypersensitivity, biological compatibility, and inhibition of certain bacteria.[2-5] They also have esthetic appeal, similar to that of composite resins, due to their off-white color. However, GICs have a significant disadvantage in their brittleness and research in improving GIC mechanical properties has been on going for decades using multiple methods.[2,3,5] Advancements are currently being widely studied to evaluate the mechanical properties of GICs, but further improvements are necessary before GICs can fully replace their amalgam counterparts.[2-10,12]

The purpose of this research was to create and evaluate more durable glass-ionomer cements by altering the mixing technique. This research seeks to evaluate mixing techniques involving a novel glass-ionomer polymer with a conventional

basic glass in order to improve the strength of GIC mechanical properties. The hypothesis was that mixing technique could produce a statistically significant difference in mechanical properties. The effect of mixing technique on mechanical properties is an important factor in that increased strength arising from technique, as opposed to chemical composition, increases the strength of all GICs, regardless of chemical components. In addition, this could allow for the incorporation of polymers that are not normally utilized in GIC formulations. Conventional glass-ionomer cements utilize a 50% aqueous polymer solution.[2] This excludes the use of polymers with rubbery domains, which could improve mechanical properties. The experimental mixing technique could allow for the incorporation of non-conventional acidic polymers that cannot be used due to solubility.

A GIC has three components: a glass, usually a basic oxide composed of calcium-fluoro-aluminosilicate (CaFAlSi), a polymer, and water.[1-4] These are then combined at a ratio of 5.4:1:1. GICs are limited to working time, about 3 minutes, in which they are malleable enough to place on a tooth or create samples used for mechanical strength tests before they harden. Typically, copolymers of acrylic acid and itaconic acid are used to for GIC polymers and the experimental polymer in this project was synthesized using itaconic acid, acrylic acid, and N-vinylpyrrolidone, with ammonium persulfate as the initiator (Figure 1). NVP was chosen as a



N-Vinyl Pyrrolidinone Acrylic Acid Itaconic Acid Ammonium Persulfate

Figure 1 *Line structure of monomers. Drawings courtesy of Dr. Scott Schricker.*

monomer because it has been found that NVP containing polyacids have improved mechanical and handling properties in addition to significantly lower contact angels and higher work adhesion in comparison to commercial Fuji II GIC.[8] In the presence of water the polymer acts as an acid, attacking the glass, releasing aluminum and calcium cations and the polyalkenoic chains can then form intra- and intermolecular salt bridges.[4] Figure 2 shows a potential interaction within a generic GIC.

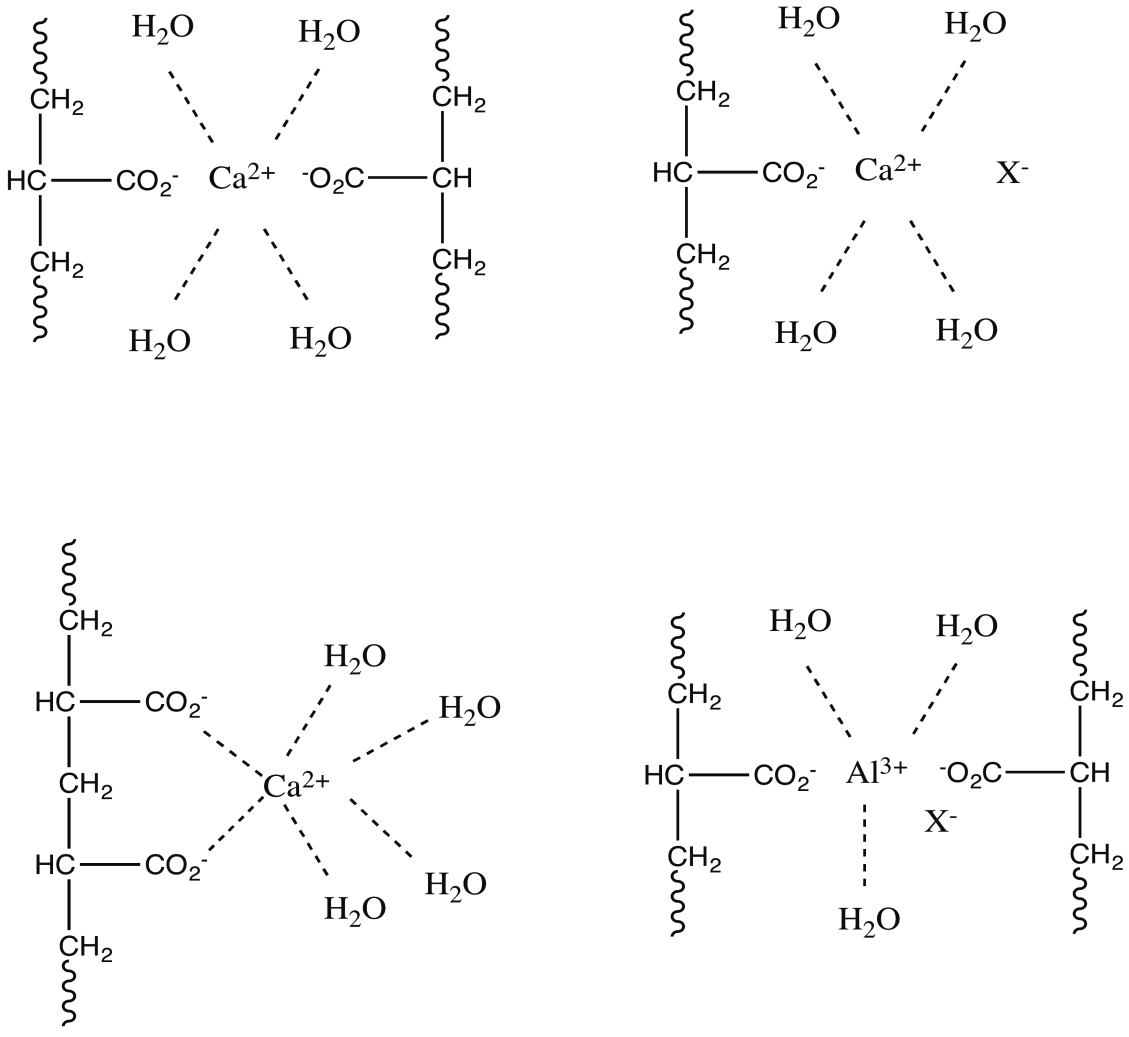


Figure 2 *Intermolecular salt bridges between polyalkenoic chains and cations. Drawings courtesy of Dr. Scott Schricker.*

2. Experimental

2.1. General

Flexural strength (FS), compression strength (CS), fracture toughness (FT), and water sorption (W_s) were evaluated for the cement made from each mixing method. FS and FT were performed using a 3-point bending test setup on a Model 4202 Instron Universal Testing Device, shown in Figure 3. CS was performed using a compression stress test setup, shown in Figure 4.

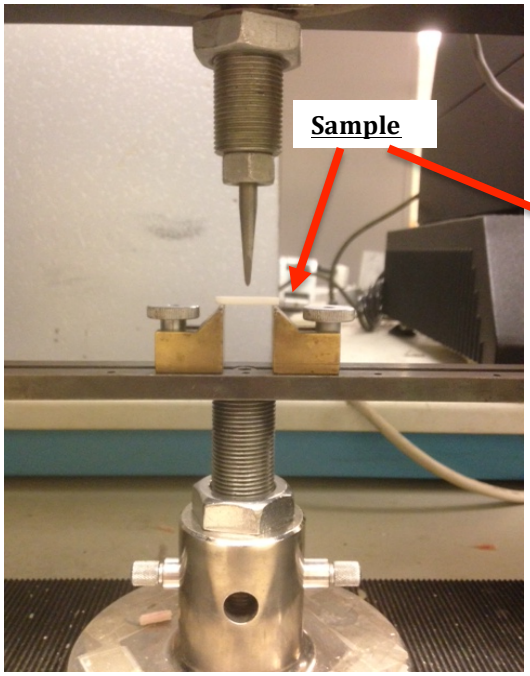


Figure 3 *Instron Universal Testing Device 3-point bending test setup*

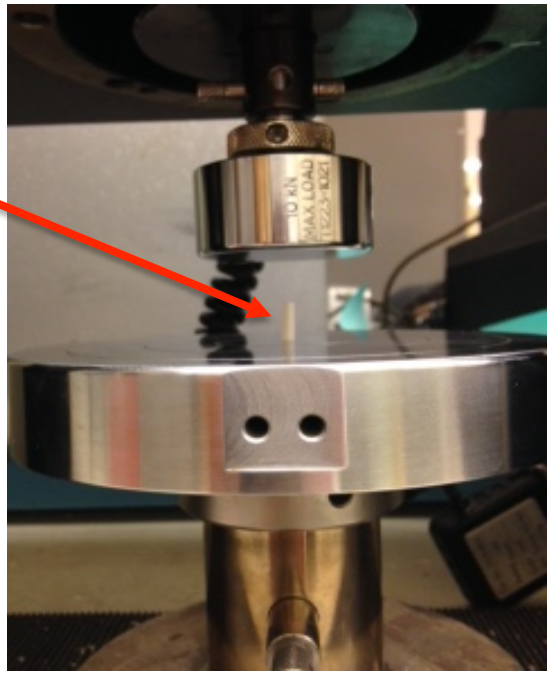


Figure 4 *Instron Universal Testing Device compression test setup*

There were two methods tested; method 1 combined the glass and polymer physically by mixing for 90 seconds in a mortar and pestle then adding water, method 2 dissolved the polymer into the water, creating a gel, and then added the glass. Method 2 is the current industry standard. In addition to these two methods, the conditioning time was also adjusted for each batch of samples using intervals of

1, 7, and 26 days. This is important as GIC's are dynamic materials that continue to condition for weeks after the initial placement.

2.2. Polymer Synthesis

Use of the same batch of polymer (ideally made during one reaction) is crucial to the value of the experiment. Since different polymers are key to the mechanical properties of the GIC, use of the same polymer allows for elimination of some outside variables with regards to structural properties of the GIC and allows the mixing technique to play a larger role in the strength of the GIC. The polymer was synthesized using a procedure previously reported by Moshaverinia et al.[8] 0.36 moles (24.7 mL) of acrylic acid, 0.045 moles (5.85 g) of itaconic acid and 0.045 moles (5 mL) of NVP were measured and dissolved in water, 0.00043 moles (0.0975 g) of ammonium persulfate were used an initiator for polymerization. The molar ratio was 8:1:1 AA:IA:NVP for the terpolymer. The reaction mixture was heated continuously at 98 °C under nitrogen for 12 h. The heating was then switched off and the reaction cooled for 1 h under nitrogen. The polymer was then lyophilized. The polymer was synthesized at 84% yield based on mass after freeze-drying.

2.3. Flexural Strength

Rectangular Bar specimens with dimensions of 2.7 mm x 2.7 mm x 25 mm were created using a plastic based mold surrounded by stainless steel. The filled mold was then pressed between two pieces of glass to cure for approximately 3 minutes. Samples were conditioned in distilled water at 37 °C then polished

unidirectionally with 320-silicone carbide sand paper. 5-6 samples were used per condition as shown in Appendix 1. The peak and break loads of the bar samples were determined using the Instron shown previously with a 1kN load cell and a 0.5 mm/min crosshead speed. The FS can then be calculated using the equation[7]:

FS = $3Pl/2bd^2$ Units = MPa

P = load at the fracture of the sample

l = distance between the supports (20 mm)

b = breadth of the sample

d = depth

2.4. Compression Strength

Cylinder shaped specimens with a radius of 4 mm and an average length of 7.5 mm were cured for approximately 3 minutes in glass tube with a radius of 4 mm. Samples were conditioned in distilled water at 37 °C then polished unidirectionally with 320-silicone carbide sand paper. 5 specimens were used per condition as shown in Appendix 1. CS was calculated using the equation[7]:

CS = $P/(\pi r^2)$ Units: MPa

P = load at the fracture of the sample

r = radius of the cylinder (4 mm)

2.5. Fracture Toughness

Rectangular Bar specimens with dimensions of 2.7 mm x 2.7 mm x 25 mm were created using the same procedure described for the FS tests then induced with

a 1 mm crack at the center of the sample. Samples were conditioned in distilled water at 37 °C. FT was calculated using the equation[11]:

$FT = (P_Q S/BW^{3/2}) \cdot f(a/W)$ Units: MPa•m$^{1/2}$

where $f(a/W) = 3(a/W)^{1/2}[1.99-(a/W)(1-a/W)\cdot(2.15-3.93a/W+2.7a^2/W^2)]/2(1+2a/W)(1-a/W)^{3/2}$

P_Q = *max load*

B = *thickness*

W = *width*

a = *crack depth (1 mm)*

Though FT testing is often reserved for metals, this method for determining FT on GICs had been used previously by Beatty and Pidaparti.[12]

2.6 Water Sorption

Rectangular Bar specimens with dimensions of 2.7 mm x 2.7 mm x 25 mm were created using the same procedure described for the FS tests. Samples were conditioned in distilled water at 37 °C. The pooled weight of the samples (5 for method 1 and 6 for method 2) was tracked over the course of 2 weeks. W_s was calculated using the equation[9]:

$(W_s) = 100 \times ((W_t - W_0)/W_0)$

W_t = *specimen weight at time t*

W_0 = *specimen initial weight*

3. Results

The mixing method produced a statistically significant difference in one mechanical test. Figures 5 shows the flexural strength comparison, Figure 6 the compression strength, Figure 7 the fracture toughness, and Figure 8 the water sorption percent change.

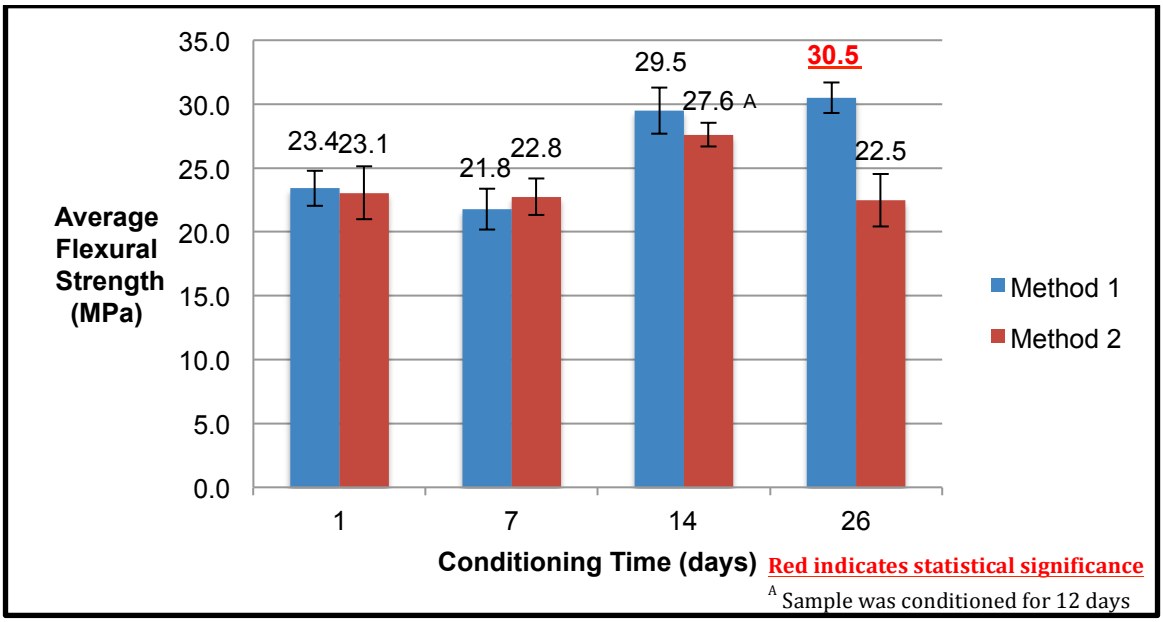


Figure 5 *Flexural Strength of Various Mixing Methods at Peak Load Over Time. Vertical Bars Indicate the Standard Error.*

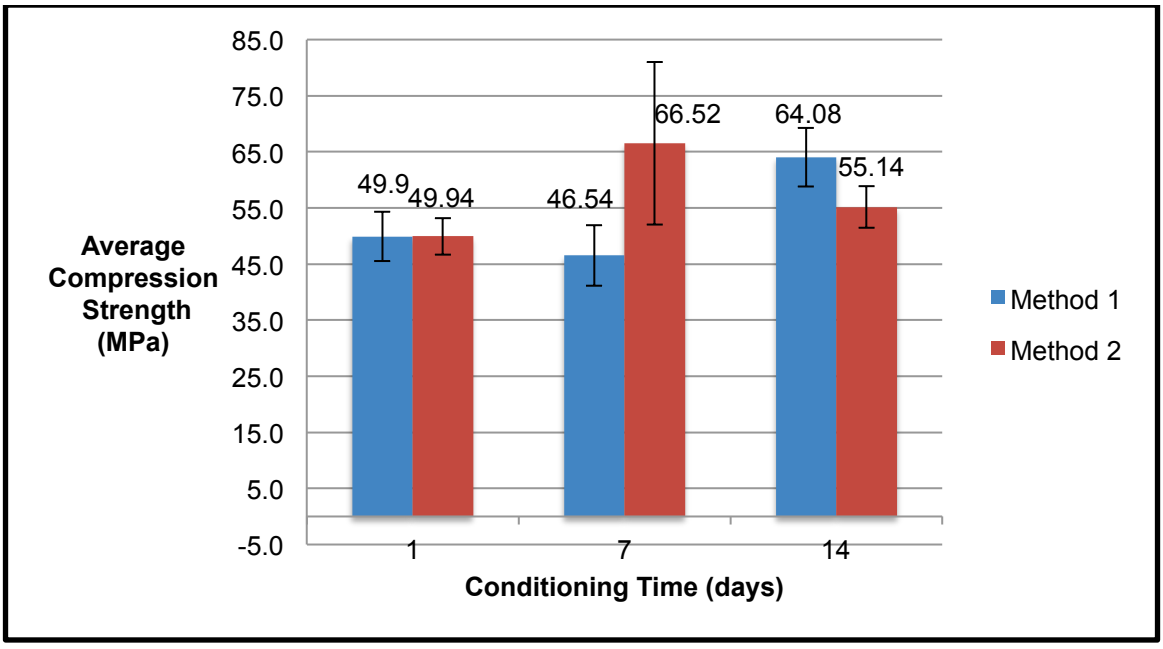


Figure 6 *Compression Strength of Various Mixing Methods at Peak Load Over Time. Vertical Bars Indicate the Standard Error.*

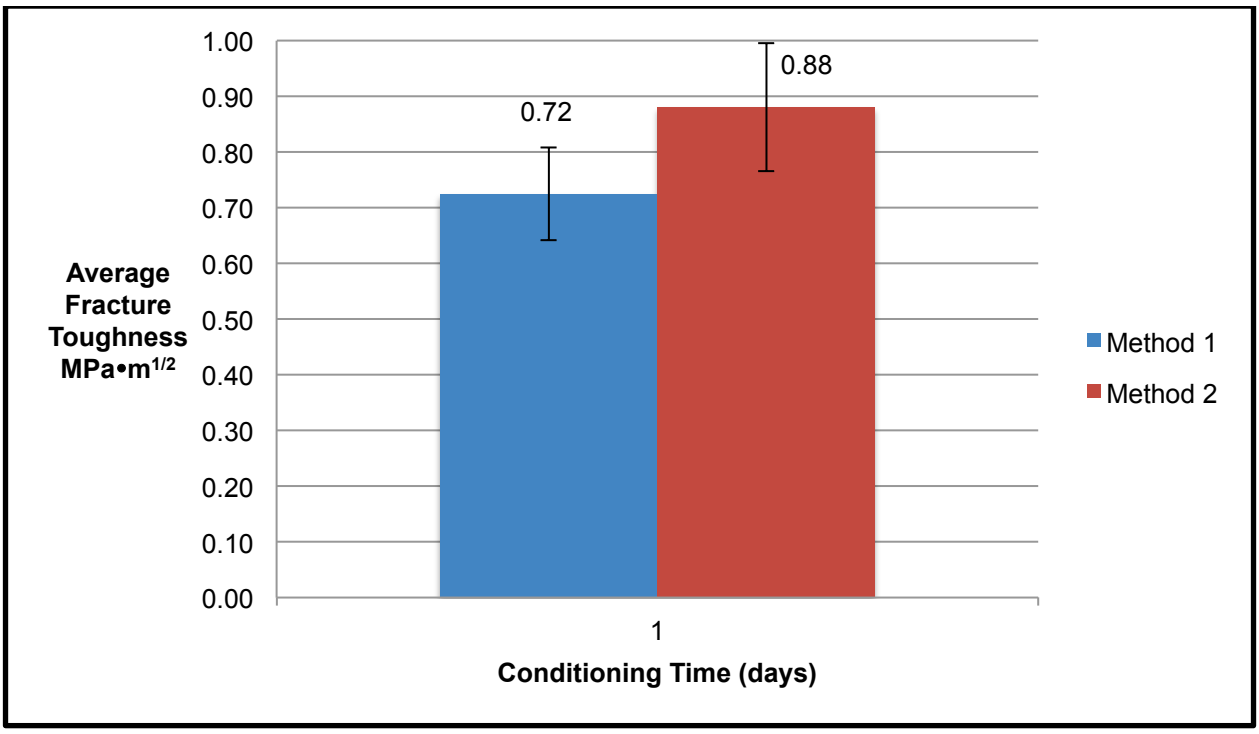


Figure 7 *Fracture Toughness of Various Mixing Methods at Peak Load Over Time. Vertical Bars Indicate the Standard Error.*

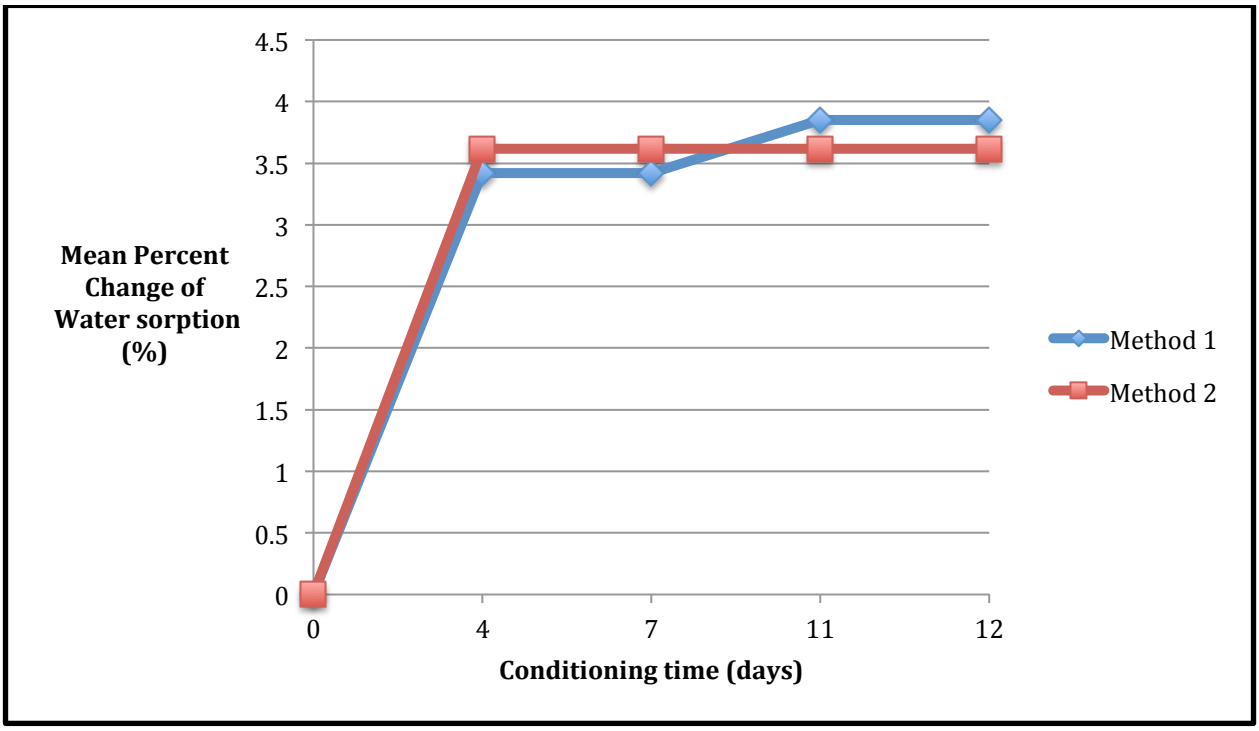


Figure 8 *Mean Percent Change of Water Sorption Using Pooled Sample Weight of Various Mixing Methods Over Time.*

A t-test was performed comparing the means of each method within each level of time with $\alpha = 0.05$ with regards to the p-value of the two-tailed distribution. Of the eight comparisons made, one result (flexural strength, 26 day) produced a statistically significant difference with method 1 being stronger than method 2 (the industry standard). In all other methods, there was no statistically significant difference. Full statistical analysis is provided in Appendix 1.

4. Discussion

The similarities in mechanical properties are not a surprising result since all the materials used were the same for each method. The statistically significant difference in flexural strength occurring at 26 days may be indicative of the idea that method 1 allows for additional strengthening of the cement over time. The trends seen in the graphs of flexural strength and compression strength support this idea and indicate that method 1 grows stronger as time goes on. The initial hypothesis of mixing technique having an effect on the structural properties was correct in one instance since one of the eight tests produced a statistically significant result. However, this may be somewhat skewed since the longest observation time was the one that produced this result. Longer conditioning times should be tested to further validate the hypothesis. The lack of difference in the strengths is an important result since method 1 and method 2 differ so greatly in mixing technique. Method 1 also provides a potentially longer shelf life than method 2 since the polymer is not degraded over time in water. Method 1 is the better choice for dental restoratives where shelf life is a critical metric, such as in space, military or emergency

situations. With the discovery of method 1 being as efficient as method 2, if not more, it provides the dental restorative community with the start to a discussion of the future of GICs. With no prior information about the mixing method question, the results indicate that additive research of novel mixing methods could provide significant impact in the field of dental restoratives. The next step could be to test mechanical properties of the GICs, using the same methods and formulations as before, but to increase conditioning time to 1 year or even 5 years. This would also give further insight into the clinical aspect of GIC longevity. The second step would be to explore novel mixing methods, such as dissolving the polymer and glass in an aprotic solvent, then removing the solvent so that the polymer and glass are not just physically bound but chemically as well.

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Appendix 1

t-Test: Two-Sample, Assuming Unequal Variances

Null Hypothesis(H_0): $\mu_1 = \mu_2$

FS 1-Day	*Method1*	*Method2*	*FS 7-Day*	*Method1*	*Method2*
Mean	23.413	23.056	Mean	21.774	[22].755
Variance	11.288	25.349	Variance	12.573	12.315
Observations	6	6	Observations	5	6
Hypothesized Mean Difference	0		Hypothesized Mean Difference	0	
df	9		df	9	
t Stat	0.145		t Stat	-0.459	
P(T<=t) one-tail	**0.444**		P(T<=t) one-tail	**0.328**	
t Critical one-tail	1.833		t Critical one-tail	1.833	
P(T<=t) two-tail	**0.888**		P(T<=t) two-tail	**0.657**	
t Critical two-tail	2.262		t Critical two-tail	2.262	
Conclusion	Cannot reject H_0		**Conclusion**	Cannot reject H_0	
FS 14-Day	*Method1*	*Method2*	*FS 26-Day*	*Method1*	*Method2*
Mean	29.527	27.519	Mean	30.502	22.469
Variance	19.790	5.203	Variance	8.495	21.232
Observations	6	6	Observations	6	5
Hypothesized Mean Difference	0		Hypothesized Mean Difference	0	
df	7		df	7	
t Stat	0.984		t Stat	3.376	
P(T<=t) one-tail	**0.179**		P(T<=t) one-tail	**0.006**	
t Critical one-tail	1.895		t Critical one-tail	1.895	
P(T<=t) two-tail	**0.358**		P(T<=t) two-tail	**0.012**	
t Critical two-tail	2.365		t Critical two-tail	2.365	
Conclusion	Cannot reject H_0		**Conclusion**	Reject H_0	*
CS 1-Day	*Method1*	*Method2*	*CS 14-Day*	*Method1*	*Method2*
Mean	49.422	49.94	Mean	46.536	66.52
Variance	95.95	53.7	Variance	146.	839.
Observations	5	5	Observations	5	4
Hypothesized Mean Difference	0		Hypothesized Mean Difference	0	
df	7		df	4	
t Stat	0.095		t Stat	1.290	
P(T<=t) one-tail	**0.464**		P(T<=t) one-tail	**0.133**	
t Critical one-tail	1.895		t Critical one-tail	2.130	
P(T<=t) two-tail	**0.927**		P(T<=t) two-tail	**0.266**	
t Critical two-tail	2.365		t Critical two-tail	2.780	
Conclusion	Cannot reject H_0		**Conclusion**	Cannot reject H_0	

CS 28-Day	*Method1*	*Method2*
Mean	64.080	55.140
Variance	137.750	69.250
Observations	5	5
Hypothesized Mean Difference	0	
df	7	
t Stat	1.389	
P(T<=t) one-tail	**0.104**	
t Critical one-tail	1.895	
P(T<=t) two-tail	**0.207**	
t Critical two-tail	2.365	
Conclusion	Cannot reject H_0	

FT 14-Day	*Method1*	*Method2*
Mean	0.725	0.881
Variance	0.028	0.053
Observations	4	4
Hypothesized Mean Difference	0	
df	5	
t Stat	1.010	
P(T<=t) one-tail	**0.161**	
t Critical one-tail	2.015	
P(T<=t) two-tail	**0.322**	
t Critical two-tail	2.571	
Conclusion	Cannot reject H_0	

WA	*Method1*	*Method2*
Mean	3.640	3.620
Variance	0.062	0.000
Observations	4	4
Hypothesized Mean Difference	0	
df	3	
t Stat	0.121	
P(T<=t) one-tail	**0.456**	
t Critical one-tail	2.353	
P(T<=t) two-tail	**0.911**	
t Critical two-tail	3.180	
Conclusion	Cannot reject H_0	

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